This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

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SAES St 909 Getter Testing at the Savannah River National Laboratory

Bench, Pilot, and Full Scale Tests

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Abstract—**Process gas tritium stripper technology has gone from catalytic oxidation followed by absorption on molecular sieve/zeolite beds to non-evaporate metal getter technology. SAES Getters produces a number of commercial getter products including St 909. St 909, a Zr-Mn-Fe alloy, is sold in pellet form, can decompose ("crack") a number of process gas impurities, and retains lower levels of tritium than other getters. The performance of this material to remove process impurities, especially methane, under of variety of operating conditions has been part of a Savannah River National Laboratory (SRNL) for five years. St 909 has been tested at the bench (6 gram) scale, the pilot (500 gram) scale, and at the full (5300) gram scale under a variety of test conditions. This paper gives a brief summary of test results obtained for the different scale tests.**

Keywords-getter; St 909; Zr-Mn-Fe; impurity; tritium; methane; carbon dioxide

I. INTRODUCTION

Over 10 years ago, Savannah River Site (SRS) tritium facilities dating back to the 1950's, were replaced with metal hydride based processes contained in controlled atmosphere glove boxes [1-3]. The glove box stripper system [1, 4-6] uses a catalytic oxidation-absorption process to minimize tritium emissions from the facility. A gas stripper system in another facility used a similar oxidation-absorption process for tritium removal from process gas streams.

In the late 1990's, a SRS project was initiated to consolidate operations from some of the older buildings into newer facilities. A new system, the Tritium Process Stripper (TPS), utilizes metal getters and diffusers to remove tritium from process waste streams without the formation of tritium oxide. A commercially available Zr-Mn-Fe alloy getter material, SAES St 909, is used in a bed at the front end of the process to getter oxygen and reduce hydrogen containing compounds to elemental hydrogen [7].

SAES St 909 was originally developed for dissociating ("cracking") tritiated water for the recovery of tritium. Zirconium based alloys $ZrMn_2$, $ZrFe_2$, $ZrCr_2$, $Zr(Mn_{0.5}Fe_{0.5})_2$, and $Zr(Mn_{0.5}Cr_{0.5})_2$ were tested for water vapor sorption rates and hydrogen "pick-up" rates and the ZrMnFe alloy chosen as the material with the best combination of water cracking rate and low hydrogen pick-up [8]. The ZrMnFe alloy was combined with an aluminum binder for pellet formation and sold as SAES St 909. St 909 was shown to crack methane, carbon monoxide, carbon dioxide, ammonia, and oxygen in helium streams [9].

St 909 was shown to react exothermically with nitrogen during ramped heating from ambient temperature to 700°C [10]. St 909 getter beds applications at SRS would have carrier gases of nitrogen, helium, and hydrogen, and methane impurities higher than those previously tested [9]. In 1999, the Savannah River National Laboratory (SRNL) started testing St 909 to determine its methane cracking performance with different methane concentrations, with different impurities, and in carrier gases of helium, hydrogen, and nitrogen. This paper gives a summary of some of the test programs using bench scale (6 gram), pilot scale (500 gram), and full scale (5300 gram) St 909 beds.

II. BENCH SCALE TESTS

To determine the impact of various process conditions on St 909 methane cracking, a flow test system, described elsewhere [11], was used for bench scale parameter screening tests. Ten, 6mm diameter by 4 mm tall St 909 pellets (6 grams) were stacked on top of one another in a bench scale test bed. The St 909 was activated for two hours by flowing 10 sccm helium through the bed and setting the heater controller to 700°C. For comparison of different tests, baseline conditions were defined as a 5% methane, which contained 1% argon as a tracer gas for Residual Gas Analyzer (RGA) analysis, a 95% helium carrier gas, a 10 sccm feed rate, a 101 kPa (760 torr) back pressure, and a temperature of 700°C.

A. Methane Cracking in a Helium Carrier

Fig. 1 shows the bed outlet methane partial pressure as a function of methane cracked/carbon gettered by the St 909, $St909_C$, for different carrier gases and tests at 700°C and 800°C. In summary, the methane cracking rate decreased as temperature decreased, the rate decreased as helium was replaced by hydrogen or nitrogen, and the rate was slowest when the carrier gas was a mixture of hydrogen and nitrogen. The methane cracking rate reduction by hydrogen and nitrogen carrier gases was described elsewhere [11].

Additional bench scale tests were conducted to examine the effect of carbon dioxide on methane cracking in helium, hydrogen, and nitrogen carrier gases. Methane and/or carbon dioxide where fed at either 2.5% or 5.0% with a helium, hydrogen, or nitrogen carrier gas. The carbon dioxide contained 1% krypton as a tracer gas for RGA analysis of carbon dioxide cracking. Some tests were also run at 800°C.
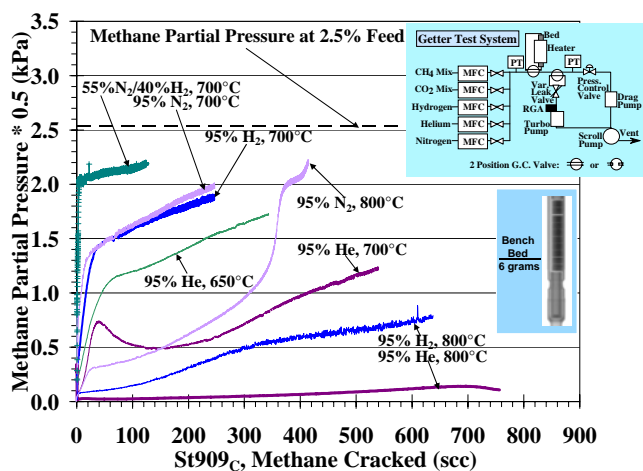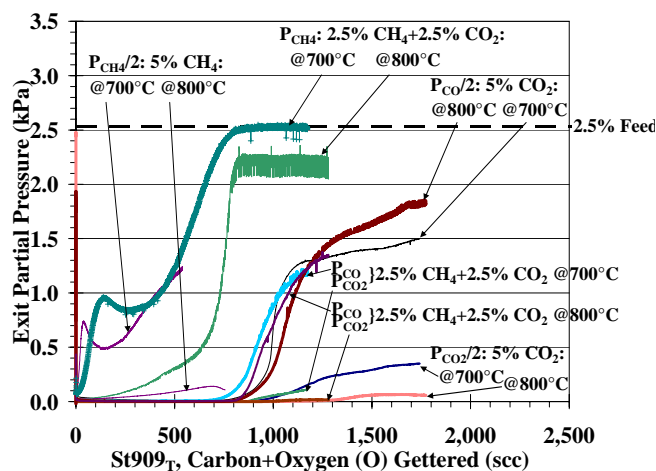
Figure 1. Bench Scale Results for 5% Methane Feed

Figure 2. Effect of CO_2 on Methane Cracking in a Helium Carrier

The effect of carbon dioxide on St 909 methane cracking in a helium carrier can be seen in Fig. 2 where bed exit methane partial pressure, P_{CH4}, is plotted versus $ST909_T$, the total carbon plus atomic oxygen gettered by the St 909. Fig. 2 shows that at low getting loadings, the carbon dioxide has some impact on methane cracking, but the effect becomes more pronounced at higher getter loadings. The methane outlet partial pressure was the same as the feed as the getter loading exceeded 800 scc at 700°C. At 800°C, methane cracking in the presence of carbon dioxide was moderately worse than without carbon dioxide until the getter loading exceeded 650 scc. After a getter loading of 650 scc, there was a rapid decrease in methane cracking rate; however, the methane cracking did not stop, but continued at some reduced rate for the duration of the test: nothing near the cracking rate without carbon dioxide.

The bed exit carbon dioxide partial pressure, P_{CO2}, and carbon monoxide partial pressure, P_{CO}, is plotted versus $ST909_T$ in Fig. 2 Fig. 2 shows carbon monoxide leaving the bed before carbon dioxide is detected. This was attributed to the removal of one oxygen atom from carbon dioxide by the St 909, but the remaining carbon monoxide molecule exits the bed before it can react with the St 909.

Tests with only carbon dioxide in the feed were run to better understand the gettering of carbon dioxide by St 909. Tests at 700°C with 2.5% and 5.0% carbon dioxide feed produced almost identical carbon oxide partial pressure versus $ST909_T$ results when the partial pressures for the 5% feed were divided by two. A test with 5% carbon dioxide feed at 800°C released less carbon dioxide and more carbon monoxide than at 700°C for St909T greater than 1,250 scc. These tests show the removal rate of the first oxygen atom from the carbon dioxide by the St 909 was increased at an increased temperature.

Fig. 2 shows methane has no measurable impact on St 909 gettering of carbon dioxide at either 700°C or 800°C in helium. Fig. 2 shows little or no methane cracking by the time carbon oxides are released from the bed indicating first oxygen removal from carbon dioxide and carbon monoxide gettering occur at rates faster than methane cracking. Running the methane/carbon dioxide tests 50% longer might produce data indicating some impact of methane on carbon dioxide cracking.

B. Methane Cracking in a Hydrogen Carrier

Fig. 3 shows the bed exit methane partial pressures with and without carbon dioxide in the hydrogen carrier gas. Carbon dioxide reacts with hydrogen to form methane. The methane formation rate was reduced when the temperature was increased to 800°C, but eventually the rate approached the 700°C formation rate. Carbon dioxide leaving the bed was almost undetectable for all tests and is indicated in Fig. 3 without identifying test conditions. Another observation during these tests was a sharp increase in the RGA water signal, as indicated in Fig. 3 as the ratio of the RGA 18-to-84 signals, before carbon monoxide was detected leaving the bed.

As before, carbon dioxide is reduced to carbon monoxide by the getter followed by the reaction of the carbon monoxide to methane and oxidation of the getter material. As St 909 loading continues, the oxygen atoms can not be removed fast enough from the surface of the St 909 and are reduced to water by the hydrogen carrier gas. At higher St 909 loadings, the St 909 can no longer decompose all of the carbon monoxide to water and methane and some is released from the bed.

C. Methane Cracking in a Nitrogen Carrier

Fig. 1 shows the drastic reduction in methane cracking rate in nitrogen compared to the rate in helium. Fig. 4 shows there is a slight difference in relative methane cracking rates for 2.5% and 5.0% methane feeds in nitrogen at 700°C. The RGA could not differentiate between carbon monoxide and nitrogen so Fig. 4 results are plotted versus methane plus carbon dioxide cracked. The methane cracking rate increased with increased temperature until a getter loading of approximately 350 scc of methane after which the bed methane partial pressure increased sharply.

Fig. 4 shows adding carbon dioxide to the feed mixture had the effect of bed methane effluents increasing to feed partial pressures at lower getter loadings than for tests without carbon dioxide. This effect was seen at 700°C and 800°C.

With carbon dioxide in the feed, raising the temperature to 800°C delayed the rapid increase in methane partial pressure

seen at 700°C, but eventually, the methane cracking rates at both 700°C and 800°C stabilized at similar, but relatively slow methane cracking rates.
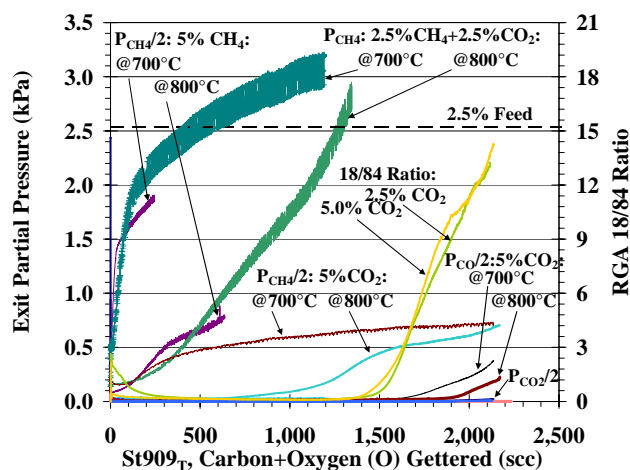

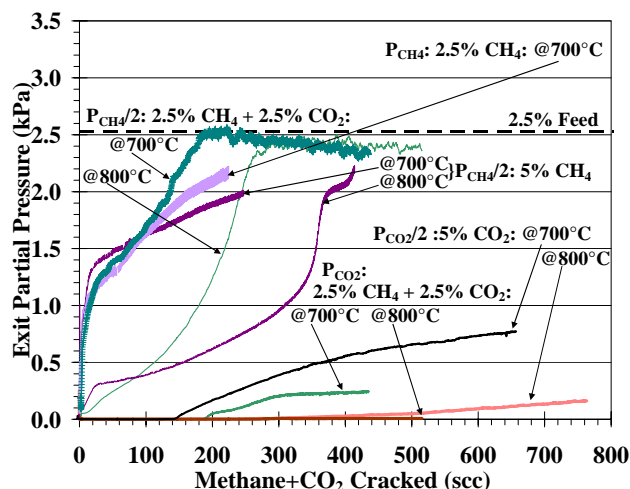Figure 3.   Effect of CO_2 on Methane Cracking in a Hydrogen Carrier

Figure 4.   Effect of CO_2 on Methane Cracking in a Nitrogen Carrier

Absent methane, relative carbon dioxide cracking rates in nitrogen were the same for 2.5% and 5.0% feeds, but Fig. 4 shows the rate for 5% feed increased greatly from 700°C to 800°C. With methane included in the feed, carbon dioxide bed effluents were also reduced as temperature increased from 700°C to 800°C. It is noted that at 700°C, carbon dioxide was detected after only 140 to 190 scc of methane plus carbon dioxide cracked compared to carbon monoxide detection during helium carrier tests occurred later after 700 scc of carbon plus atomic oxygen were gettered.

III.   PILOT SCALE TESTING

Bench scale tests are good for screening material performance, but 500 gram (pilot-scale) tests were run to better estimate full scale bed performance. The beds were fabricated using Whitey® 150 cm³ sample cylinders, activated by a 100 sccm argon purge while vertical, three-zone furnace was

ramped at 2.5°C per minute to 700°C. Four pilot tests were run with 20% hydrogen, different feed gas impurity compositions with a balance of helium, 30 sccm feed, 203 kPa (1520 torr) back-pressure, and 700°C. A gas chromatograph (GC) was used for ppm level detection of methane. Test 1 had 2.5% methane feed, Test 2 had 1.1% methane with 1.4% carbon dioxide, Test 3 had 1.1% methane with 2.1% nitrogen, and Test 4 had 1.1% methane with 0.4% nitrogen. Figure 5 shows the bed methane outlet concentration as a function of time.
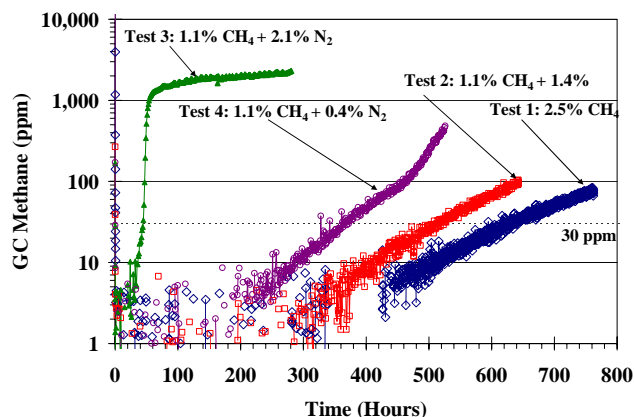

Figure 5.   Pilot Scale St 909 Results Versus Time

The amount of methane, carbon dioxide and nitrogen gettered were calculated when the bed effluent reached 30 ppm methane. The "methane impurity equivalence", the amount of carbon dioxide or nitrogen that gave the equivalent impact on methane getter break-through at 30 ppm, was calculated to be 1.59 moles methane per mole carbon dioxide for Test 2, 15.6 moles methane per mole of nitrogen for Test 3, and 8.15 moles methane per mole of nitrogen for Test 4. Figure 6 shows the methane outlet concentration for the four tests versus equivalent methane cracked.

Figure 7 shows the bed outlet concentration versus time for Test 4. Test 4, as well as Test 3, showed the methane outlet concentrations below 30 ppm could be reestablished if the nitrogen supply to the bed was stopped. Figure 7 also shows the methane cracking performance could be quickly restored after a loss of a heater zone or loss of power once the entire bed was brought back to its operating temperature. Addition of 200 ppm water to the bed feed gas did not measurably alter methane cracking performance. Addition of carbon dioxide to the feed late in the test had essentially the same effect as adding it at the start of the test. Stopping the hydrogen flow at the end of the test produced a decrease in methane concentration supporting the bench scale conclusions that hydrogen suppresses the methane decomposition/gettering rate. Addition of nitrogen late in Test 3 had essentially the same effect as when it was added at the start of the test.

IV.   FULL SCALE TESTING

Full scale beds contain nominally 5300 grams of St 909. A bed is placed in a single zone furnace and the feed gas warmed as it flows through the outer bed jacket before entering the bottom of the bed. Flow is exhausted out the top of the bed.
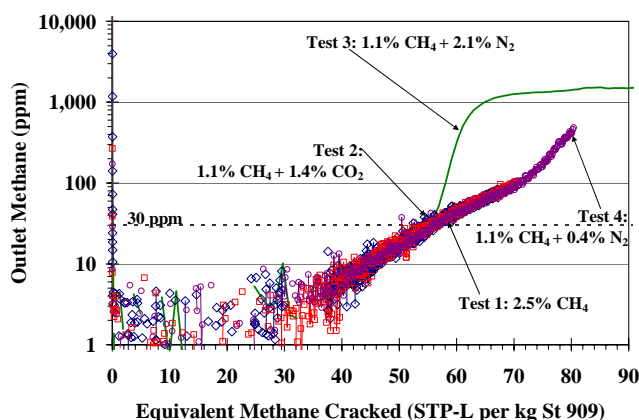
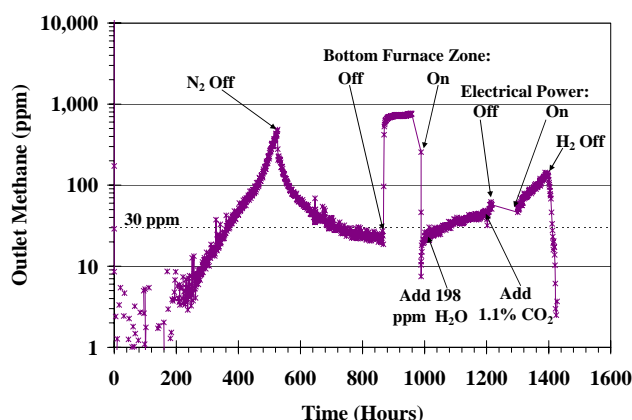Figure 6. Pilot Scale Results Versus Equivalent Methane Gettered

Figure 7. Complete Test 4 Results

A. Nitrogen Carrier Gas Tests

A full scale (5370 gram) St 909 bed was extensively tested after saturating the bed with 395 STP-L of nitrogen [12]. Tests to decompose/crack oxygen, water, carbon dioxide, and methane were done at 600°C, 700°C, and 750°C. The testing showed a range of cracking efficiencies for oxygen, water, and carbon dioxide at different test conditions. Consistent with the bench and pilot scale results, no methane cracking was observed at 600°C and methane cracking efficiencies varied between 10 to 50% at 700°C [12].

B. 20% Hydrogen, Balance HeliumCarrier Gas Tests

A full scale (5300 gram) production style St 909 bed was tested to verify the results obtained from pilot scale Test 1. The test was run using Pilot Test 1 conditions with ten times the gas feed rated. The 69 hour test found no detectable methane emissions event though poor insulation at the top of the bed kept the top thermowell temperature at 550°C instead of the body temperature of 700°C.

V. CONCLUSIONS

Bench scale St 909 tests give relatively fast, inexpensive results on St 909 methane cracking performance under different test conditions. Pilot scale St 909 tests give a better representation of St 909 performance in a full scale bed for a given set of test conditions. Full scale tests give the best prediction of bed performance due to better representation of temperature gradients the bed will experience in a process environment. Tests on full scale production vessels also demonstrate the effect of pellet swelling on bed flow characteristics and are a necessary part of technology development before fielding new technology into a tritium process.

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